Safe Water Technology for Arsenic Removal

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Abstract

Arsenic contamination of drinking water has been reported from many parts of world. In some arsenic affected areas, substitution of drinking water source by a safe and easily available one may not be possible during part or all of the year, or may be very expensive. Arsenic removal may be a more appropriate water supply option in these situations. This paper describes some safe water technologies for arsenic removal.

Coagulation is the most common arsenic removal technology. As many Bangladesh waters contain arsenite, oxidation with chlorine or permanganate is required first. Coagulation with ferric chloride works best at pH below 8. Alum has a narrower effective range, from pH 6-8. Ion exchange resins are commercially produced synthetic materials that can remove some compounds from water. These resins only remove arsenate. Activated alumina, like ion exchange resins, is commercially available in coarse grains. Activated alumina beds usually have much longer run times than ion exchange resins, typically several tens of thousands of beds can be treated before arsenic breakthrough. Activated alumina works best in slightly acidic waters (pH 5.5 to 6). Membrane methods for arsenic removal include reverse osmosis and nanofiltration. Currently available membranes are more expensive than other arsenic removal options, and are more appropriate in municipal settings, where very low arsenic levels are required. Other techniques exist for arsenic removal, but are less well documented. When arsenic-rich water also contains high levels of dissolved iron, iron removal will also remove much of the arsenic. Introduction of zero-valent iron filings in three-pitcher filters to treat water in the home is showing great *promise. Many new materials are being tested for arsenic removal, from low-tech iron-coated sand and greensand to specially engineered synthetic resins.*

In all cases, technologies should meet several basic technical criteria. The biggest challenges ahead lie however in applying the technologies described in poor, rural settings, and in enabling those communities to choose safe sources of water for drinking and cooking.

INTRODUCTION

In areas where the drinking water supply contains unsafe levels of arsenic, the immediate concern is finding a safe source of drinking water. There are two main options: finding a new safe source, and removing arsenic from the contaminated source. In either case, the drinking water supplied must be free from harmful levels of arsenic, but also from bacteriological contamination, and other chemical contaminants. This paper reviews available technologies for arsenic removal.

When arsenic contamination is identified, the immediate priority must be to find a safe alternate source of drinking and cooking water for affected communities. Alternate sources must be not only arsenic-free, but also microbiologically safe – it would be a serious mistake to revert back to unsafe use of surface water sources. In some cases, there may be no one technology that can provide communities with a sustainable, continuous, affordable, safe water supply. If a year-round safe water source is not currently available, it may be necessary as a short-term solution to use one source during wet seasons (e.g. groundwater, rainwater) and another during dry seasons (e.g. removing arsenic from contaminated water). If a completely satisfactory, arsenic-free water source cannot be established, the short-term goal should be to reduce arsenic levels in drinking water as much as possible, as quickly as possible, even if regulatory standards cannot be immediately met. It should be recalled that health effects of arsenic are dose-dependent, and a partial solution is better than no solution. The implementation of a temporary solution should not be used as a reason to delay design and implementation of a long-term plan.

In all cases, technologies should meet several basic technical criteria. Water supply options must first of all be able to produce water of the required quality, both chemical and bacteriological. Systems should also be able to supply water in adequate quantity, throughout different seasons. Technologies should be robust. It is important that operational safety be ensured. Finally, technologies should not have an undue adverse effect on the environment.

Technologies meeting these technical criteria can be evaluated under several socioeconomic criteria. First, the systems must be economically feasible. Introduction of new technologies requires institutional capacity including production and delivery of materials, training, and quality control monitoring. New options must be convenient, or people will not use them. Gender impacts should be considered, so that the workload of women and girls is not unduly increased. New technologies require behavioral change on the part of the user, thus communication interventions should be considered. Finally, technologies must be socially acceptable to community members in order to be successful as a long-term safe water supply option.

TECHNOLOGIES FOR ARSENIC REMOVAL

In some areas, arsenic-contaminated water will be abundant, and arsenic-free sources scarce or polluted with other compounds. In these areas it may be most efficient to remove arsenic from the contaminated water, at least as a short term measure. Many technologies have been developed for the removal of arsenic. Most of the documented experience has been with large municipal treatment plants, but some of the same technologies can be applied at community or household levels.

All of the technologies for arsenic removal rely on a few basic chemical processes, which are summarized below:

- Oxidation/reduction: reactions that reduce (add electrons to) or oxidize (remove electrons from) chemicals, altering their chemical form. These reactions do not remove arsenic from solution, but are often used to optimize other processes.
- Precipitation: Causing dissolved arsenic to form a low-solubility solid mineral, such as calcium arsenate. This solid can then be removed through sedimentation and filtration. When coagulants are added and form flocs, other dissolved compounds such as arsenic can become insoluble and form solids, this is known as coprecipitation. The solids formed may remain suspended, and require removal through solid/liquid separation processes, typically coagulation and filtration.
- Adsorption and ion exchange: various solid materials, including iron and aluminum hydroxide flocs, have a strong affinity for dissolved arsenic. Arsenic is strongly attracted to sorption sites on the surfaces of these solids, and is effectively removed from solution. Ion exchange can be considered as a special form of adsorption, though it is often considered separately. Ion exchange involves the reversible displacement of an ion adsorbed onto a solid surface by a dissolved ion. Other forms of adsorption involve stronger bonds, and are less easily reversed.
- Solid/liquid separation: precipitation, co-precipitation, adsorption, and ion exchange all transfer the contaminant from the dissolved to a solid phase. In some cases the solid is large and fixed (e.g. grains of ion exchange resin), and no solid/liquid separation is required. If the solids are formed *in situ* (through precipitation or coagulation) they must be

separated from the water. Gravity settling (also called sedimentation) can accomplish some of this, but filtration is more effective. Most commonly, sand filters are used for this purpose.

- Physical exclusion: some synthetic membranes are permeable to certain dissolved compounds but exclude others. These membranes can act as a molecular filter to remove dissolved arsenic, along with many other dissolved and particulate compounds.
- Biological removal processes: bacteria can play an important role in catalyzing many of the above processes. Relatively little is known about the potential for biological removal of arsenic from water.
- Boiling does not remove arsenic from water.

Most of the established technologies for arsenic removal make use of several of these processes, either at the same time or in sequence. All of the removal technologies have the added benefit of removing other undesirable compounds along with arsenic – depending on the technology, bacteria, turbidity, color, odor, hardness, phosphate, fluoride, nitrate, iron, manganese, and other metals can be removed.

Historically, the most common technologies for arsenic removal have been coagulation with metal salts, lime softening, and iron/manganese removal. Since the WHO Guideline Value for arsenic in drinking water was lowered from 50 to 10 µg/L in 1993, several countries have lowered their drinking water standards, in some cases to 10 µg/L. In January 2001, the USEPA lowered the U.S. drinking water standard from 50 to 10 µg/L(only to postpone/reconsider this decision a few months later).

Coagulation processes are sometimes unable to efficiently remove arsenic to these low levels. As a result, various alternate technologies have been developed or adapted that are capable of removing arsenic to trace levels. These advanced treatment options include ion exchange, activated alumina, and membrane methods such as reverse osmosis and nanofiltration. While these technologies have all been shown to be effective in lab or pilot studies, there is still relatively little experience with full-scale treatment. In addition, a number of novel removal technologies are under development, some of which show great promise.

The main arsenic removal technologies are presented below, along with a brief description of how removal efficiency is affected by arsenic concentration and speciation, pH, and the presence of other dissolved constituents.

Oxidation

Most arsenic removal technologies are most effective at removing the pentavalent form of arsenic (arsenate), since the trivalent form (arsenite) is predominantly non-charged below pH 9.2 Therefore, many treatment systems include an oxidation step to convert arsenite to arsenate. Oxidation alone does not remove arsenic from solution, and must be coupled with a removal process such as coagulation, adsorption or ion exchange.

Arsenite can be directly oxidized by a number of other chemicals, including gaseous chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide, and Fenton's reagent (H_2O_2/Fe^{2+}). Some solids such as manganese oxides can also oxidize arsenic. Ultraviolet radiation can catalyze the oxidization of arsenite in the presence of other oxidants, such as oxygen. Direct UV oxidation of arsenite is slow, but may be catalyzed by the presence of sulfite (Ghurye and Clifford, 2000), ferric iron (Emett and Khoe, 2001) or citrate (EAWAG, 1999). Chlorine is a rapid and effective oxidant, but may lead to reactions with organic matter, producing toxic trihalomethanes as a by-product. Chlorine is widely available globally, though if improperly stored it can lose its potency rapidly.

In Europe, and increasingly in the USA, ozone is being used as an oxidant. In developing countries, ozone has not been widely used. An ozone dose of 2 mg/L, contacted with the water for 1 minute prior to filtration, has been shown to be effective in oxidizing iron and manganese, at the same time removing arsenic and other metals to below detection limits (Nieminski and Evans, 1995). At a similar ozone dose, arsenite was shown to have a half-life of approximately 4 minutes (Kim and Nriagu, 2000). Ozone is also a potent disinfectant, but unlike chlorine, does not impart a lasting residual to treated water.

Permanganate effectively oxidizes arsenite, along with Fe(II) and Mn(II). It is a poor disinfectant, though it can produce a bacteriostatic effect. Potassium permanganate ($KMnO_4$) is widely available in developing countries, where it is used as a topical antibiotic for minor cuts. It is relatively stable with a long shelf life. Residual manganese in treated water should not exceed the WHO guideline of 0.5 mg/L (WHO, 1993). Hydrogen peroxide may be an effective oxidant if the raw water contains high levels of dissolved iron, which often occur in conjunction with arsenic contamination.

Coagulation and Filtration

The most heavily documented treatment methods for arsenic removal involve coagulation and filtration, either using metal salts or lime softening. This treatment can effectively remove many suspended and dissolved constituents from water besides arsenic, notably turbidity, iron, manganese, phosphate and fluoride. Significant reductions are also possible in odor, color, and potential for trihalomethane formation. Thus coagulation and filtration to remove arsenic will improve other water quality parameters, resulting in ancillary health and esthetic benefits. However, the optimal conditions vary for removal of different constituents, and coagulation to remove arsenic may not be optimal for removal of other compounds, notably phosphate and fluoride.

Arsenic removal with metal salts has been shown since at least 1934

(Buswell, 1943). The most commonly used metal salts are aluminum salts such as alum, and ferric salts such as ferric chloride or ferric sulfate. Ferrous sulfate has also been used, but is less effective (Jekel, 1994; Hering et al., 1996; Hering et al., 1997). Excellent arsenic removal is possible with either ferric or aluminum salts, with laboratories reporting over 99% removal under optimal conditions, and residual arsenic concentrations of less than 1 μg/L (Cheng et al., 1994). Full-scale plants typically report a somewhat lower efficiency, from 50% to over 90% removal.

During coagulation and filtration, arsenic is removed through three main mechanisms (Edwards, 1994):

- precipitation: the formation of the insoluble compounds $Al(AsO_4)$ or $Fe(AsO_4)$
- coprecipitation: the incorporation of soluble arsenic species into a growing metal hydroxide phase
- adsorption: the electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxide.

All three of these mechanisms can independently contribute towards contaminant removal. In the case of arsenic removal, direct precipitation has not been shown to play an important role. However, coprecipitation and adsorption are both active arsenic removal mechanisms.

Numerous studies have shown that filtration is an important step to ensure efficient arsenic removal. After coagulation and simple sedimentation, HAO and HFO – along with their sorbed arsenic load – can remain suspended in colloidal form. Hering and others showed that coagulation and sedimentation without filtration achieved arsenate removal efficiencies of 30%; after filtration through a 1.0 micron filter, efficiency was improved to over 96%. Only marginal improvements were made by reducing the filter size to 0.1 micron (Hering et al., 1996). In field applications, some plants improve arsenic removal with two-stage filtration (Sancha, 1999b).

Ion-Exchange Resins

Synthetic ion exchange resins are widely used in water treatment to remove many undesirable dissolved solids, most commonly hardness, from water. These resins are based on a cross-linked polymer skeleton, called the ‘matrix’. Most commonly, this matrix is composed of polystyrene cross-linked with divinylbenzene. Charged functional groups are attached to the matrix through covalent bonding, and fall into four groups (Clifford, 1999):

- Strongly acidic (e.g. sulfonate, $–SO_3^-$)
- Weakly acidic (e.g. carboxylate, $–COO^-$)
- Strongly basic [e.g. quaternary amine, $–N^+(CH_3)_3$]
- Weakly basic [e.g. tertiary amine, $–N(CH_3)_2$]

The acidic resins are negatively charged, and can be loaded with cations (e.g. Na^+), which are easily displaced by other cations during water treatment. This type of cation exchange is most commonly applied to soften hard waters. Conversely, strongly basic resins can be pretreated with anions, such as Cl^-, and used to remove a wide range of negatively charged species. Clifford gives the following relative affinities of some common anions for a type 1 strong-base anion resins (Clifford, 1999):

$$CrO_4^{2-} >> SeO_4^{2-} >> SO_4^{2-} >> HSO_4^- > NO_3^- > Br^- > HAsO_4^{2-} > SeO_3^{2-} > HSO_3^{3-} > NO_2^- > Cl^-$$

Different resins will have differing selectivity sequences, and resins have been developed specifically to optimize removal of sulfate, nitrate, and organic matter. Various strong-base anion exchange resins are commercially available which can effectively remove arsenate from solution, producing effluent with less than 1 µg/L arsenic. Arsenite, being uncharged, is not removed. Analysts have taken advantage of this specificity to develop procedures for analytical differentiation of arsenite and arsenate (e.g. Ficklin, 1983; Edwards et al., 1998). Therefore, unless arsenic is present exclusively as arsenate, an oxidation step will be a necessary precursor to arsenic removal.

Conventional sulfate-selective resins are particularly suited for arsenate removal. Nitrate-selective resins also remove arsenic, but arsenic breakthrough occurs earlier. Most commonly, resins are pretreated with hydrochloric acid, to establish chloride ions at the surface, which are easily displaced by arsenic (Ghurye et al., 1999), though the resin can be primed with other anions such as bromide or acetate (Edwards et al., 1998). Packed beds are commonly designed to have an Empty Bed Contact Time (EBCT) of 1.5 to 3 minutes.

Arsenate removal is relatively independent of pH and influent concentration. On the other hand, competing anions, especially sulfate, have a strong effect. The number of bed volumes that can be treated before arsenic breakthrough (defined as 10% of the influent concentration) can be roughly estimated with two simple formulas: (Clifford and Majano, 1993; cited in Chen et al., 1999).

$$\text{For } [SO_4^{\ 2-}] < 120 \text{ mg/L: Bed Volumes} = -606 * \ln[SO_4^{\ 2-}] + 3{,}150$$
$$\text{For } [SO_4^{\ 2-}] > 120 \text{ mg/L: Bed Volumes} = -200 * \ln[SO_4^{\ 2-}] + 1{,}250$$

where $[SO_4^{\ 2-}]$ is the initial sulfate concentration in mg/L. In low-sulfate waters, ion exchange resin can easily remove over 95% of arsenate, and treat from several hundreds to over a thousand bed volumes before arsenic breakthrough occurs. Accordingly, the USEPA recommends that ion exchange resins not be used in waters with >120 mg/L sulfate or >500 mg/L TDS, and will be most effective in waters with even lower sulfate levels (<25 mg/L) (USEPA, 2000).

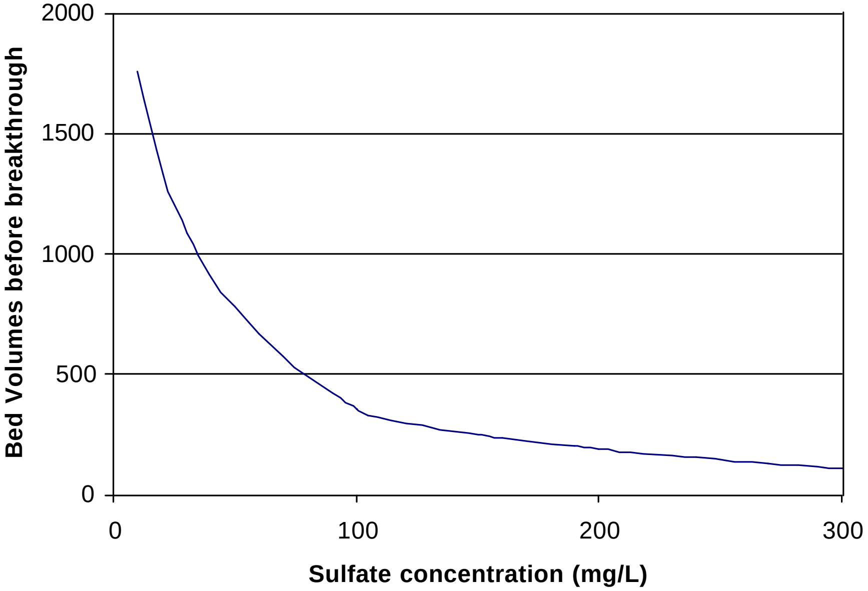


Figure 1 : Bed volumes treated with ion exchange resin

Ion exchange capacity, analogous to the adsorption capacity discussed in the previous section, is a measure of the number of exchange sites, and is usually measured in milliequivalents (meq) per mL (wet volume, including pore spaces. The operating capacity measures actual performance of resins under environmental conditions, and is always less than the advertised exchange capacity, due to incomplete regeneration and contaminant leakage.

Activated Alumina

Activated alumina is a granulated form of aluminum oxide (Al_2O_3) with very high internal surface area, in the range of 200-300 m^2/g. This high surface area gives the material a very large number of sites where sorption can occur, and activated alumina has been widely used for removal of fluoride. In the early 1970s Bellack accidentally discovered that activated alumina could remove arsenic from water (Bellack, 1971; Sorg and Logsdon, 1978).

The mechanisms of arsenic removal are similar to those of a weak base ion exchange resin, and are often collectively referred to as ‘adsorption’, though ligand exchange and chemisorption are technically more appropriate terms (Clifford, 1999). The kinetics of arsenic removal onto the alumina surface are slower than those of ion exchange resins, and some arsenic leakage is often noted in activated alumina systems.

Arsenic removal efficiency is excellent (typically > 95%), for both arsenate and arsenate, but arsenic capacity varies significantly, and is controlled primarily by pH and influent arsenic concentration and speciation. Arsenate removal capacity is best in the narrow range from pH 5.5 to 6.0, where the alumina surfaces are protonated, but acid anions are not yet concentrated enough to compete with arsenic for sorption sites (Trussell et al., 1980; Rosenblum and Clifford, 1984; Clifford, 1999). Typically, activated alumina has a point of zero charge (PZC), below which the surface is positively charged, and above which the surface bears a negative charge, at pH 8.2. Arsenic removal capacity drops sharply as the PZC is approached, and above pH 8.5, is reduced to only 2-5% of capacity at optimal pH (Clifford, 1999). For neutral and basic waters, therefore, pH adjustment may be necessary for effective arsenic removal.

Fine (28-48 mesh) particles of activated alumina are typically used for arsenic removal, with an Empty Bed Contact Time of five to eight minutes (Rubel and Woosely, 1979). When operated in the optimal pH range, activated alumina beds have much longer run times than ion exchange resins. The number of bed volumes that can be treated at optimal pH before arsenate breaks through is mainly controlled by the influent arsenic concentration

Frank and Clifford reported an arsenate capacity (at pH 6) of about 1.6 g/L of activated alumina, consistent with an earlier reported capacity of 4 mg/g, assuming a bulk density of 0.5 kg/L (Gupta and Chen, 1978). Fox reported a somewhat lower capacity of 1 mg/g, but this is likely due to the elevated pH (7.4-8.0) of the influent water (Fox, 1989).

The sorption sites on the activated alumina surface are also attractive to a number of anions other than arsenate: Clifford reports the selectivity sequence of activated alumina in the pH range of 5.5 to 8.5 as (Clifford, 1999):

$$OH^- > H_2AsO_4^- > Si(OH)_3O^- > HSeO_3^- > F^- > SO_4^{2-} > CrO_4^{2-} >> HCO_3^- > Cl^- > NO_3^- > Br^- > I^-$$

Trussell and others reported a similar selectivity sequence, but included phosphate as the second most preferred anion, after hydroxyl, and placed fluoride above arsenate in the sequence (Trussell et al., 1980). Because of activated alumina's strong selectivity for arsenate, competing anions pose less of a problem than with ion exchange resins. Sulfate, and to a lesser extent, chloride, have been shown to reduce capacity, but the competition effect is not as dramatic as with ion exchange resins (Rosenblum and Clifford, 1984). Phosphate and fluoride are also sorbed onto activated alumina, producing improvements in drinking water quality, but at the same time reducing arsenic removal potential.

Activated alumina can be regenerated by flushing with a solution of 4% sodium hydroxide, which displaces arsenic from the alumina surface, followed by flushing with acid, to re-establish a positive charge on the grain surfaces.

Regeneration is more difficult, and less complete (generally 50-80%) than with ion exchange resins (Clifford, 1986).

The advantages of activated alumina are that simple removal systems can be developed at community or household levels that require no chemical addition. Since activated alumina can treat thousands of bed volumes before breakthrough, filters could be operated for months before the media need to be changed or regenerated. Activated alumina will also remove selenite, fluoride, sulfate, and chromate. Disadvantages include the possibility that the media will be fouled or clogged by precipitated iron, the relatively narrow pH range for optimal operation, and the relative difficulty of regeneration. Also, compared with ion exchange resins, a significantly longer Empty Bed Contact Time is required.

Membrane Methods

Synthetic membranes are available which are selectively permeable: the structure of the membrane is such that some molecules can pass through, while others are excluded, or rejected. Membrane filtration has the advantage of removing many contaminants from water, including bacteria, salts, and various heavy metals.

Two classes of membrane filtration can be considered: low-pressure membranes, such as microfiltration and ultrafiltration; and high-pressure membranes such as nanofiltration and reverse osmosis. Low-pressure membranes have larger nominal pore sizes, and are operated at pressures of 10-30 psi. The tighter high-pressure membranes are typically operated at pressures from 75 to 250 psi, or even higher (Letterman, 1999).

From Figure 2, it is clear that reverse osmosis (RO) and nanofiltration (NF) membranes have pore sizes appropriate for removal of dissolved arsenic, which is in the ‘metal ion’ size range. Both RO and NF membranes are most often operated in lateral configurations, in which only a small amount of the raw water (10-15%) passes through the membrane as permeate. In household systems, where only a small amount of treated water is required for cooking and drinking, this low recovery rate may be acceptable. Municipal systems achieve higher recovery rates (80 to over 90%) by using multiple membrane units in series.

In recent years, a new generation of RO and NF membranes have been developed that are less expensive and operate at lower pressures, yet allow improved flux and are capable of efficient rejection of both arsenate and arsenite. Waypa and others have showed that some of the new membranes, operated at pressures ranging from 40-400 psi, were able to reject from 96-99% of both arsenate and arsenite in spiked natural waters. The authors attribute this rejection of arsenite to the relatively large molecular weight of both arsenate and arsenic, rather than charge repulsion. At these high arsenic rejection rates, membrane filtration can result in extremely low arsenic levels in treated water.

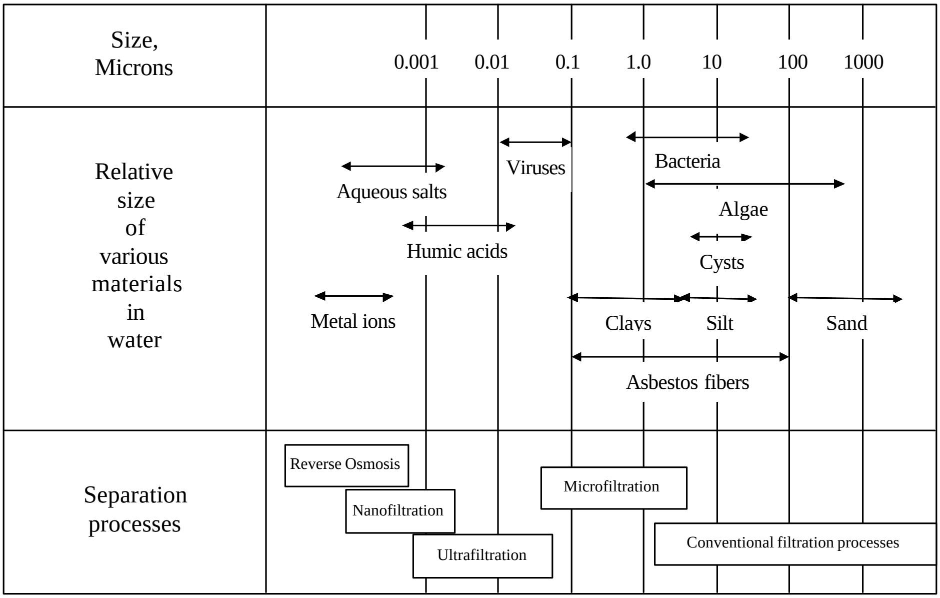


Figure 2 : Pore size of various membranes, and size of materials subject to filtration (Redrawn after Letterman, 1999)

Arsenic removal was found to be independent of pH and the presence of co-occurring solutes, but was somewhat improved at lower temperatures. Interestingly, the NF membrane tested performed comparably to the RO membranes, even though the operating pressure was much lower (40-120 psi, compared to 200-400 psi) (Waypa et al., 1997). Membrane filtration requires a relatively high-quality influent water. Membranes can be fouled by colloidal matter in the raw water, particularly organic matter. Iron and manganese can also lead to scaling and membrane fouling. To prevent fouling, reverse osmosis filters are almost always preceded by a filtration step.

Membrane filtration has the advantage of lowering the concentrations of many other components in addition to arsenic. Even ultrafiltration (UF) membranes are able to remove over 99.9% of bacteria, *Giardia* and viruses. Also, the membrane itself does not accumulate arsenic, so disposal of used membranes would be simple. Operation and maintenance requirements are minimal: no chemicals need be added, and maintenance would consist of ensuring a reasonably constant pressure, and periodically wiping the membrane clean. The main disadvantages are low water recovery rates (typically only 10-20% of the raw water passes through the membrane), the need to operate at high pressures, relatively high capital and operating costs, and the risk of membrane fouling. Also, particularly with RO, the treated water has very low levels of dissolved solids, and can be very corrosive, and deficient in minerals which can be important micronutrients for humans.

Emerging Technologies

In recent years, a tremendous amount of research has been conducted to identify novel technologies for arsenic removal, particularly low-cost, low-tech systems that can be applied in rural areas. Most of these technologies rely on oxidation of arsenite, followed by filtration through some sort of porous material, where arsenic is removed through adsorption and coprecipitation. Many of these systems make use of iron compounds, which have a very strong affinity for arsenic. A brief review of some of the most documented technologies is given below.

Fe-Mn Oxidation

Conventional iron and manganese removal can result in significant arsenic removal, through coprecipitation and sorption onto ferric or manganic hydroxides. The mechanisms involved are the same as in coagulation and filtration. Most low-cost technologies for arsenic and manganese removal rely on aeration and filtration through porous media such as sand and gravel. Any technology that effectively removes iron and manganese could be evaluated to see if arsenic is also removed effectively. In this respect arsenic removal is more convenient than that of fluoride, which does not undergo oxidation, and is not removed by coprecipitation with iron.

In Bangladesh and West Bengal, elevated arsenic concentrations are often associated with high iron and manganese levels. One survey in Bangladesh found that over 80% of arsenic-affected tubewells (>50 µg/L) also contained iron levels of 2 mg/L or more. However, iron alone is not a good indicator of arsenic: 30% of the wells with safe levels of arsenic also had 2 mg/L iron or more (DPHE/BGS/MML, 1999). Because of the link between arsenic and iron levels, and the affinity of arsenic for iron hydroxides, there have been calls for a simple solution to arsenic contamination: simple storage of pumped water to allow iron to settle out, scavenging arsenic in the process. While this is an appealing idea, successful application of this type of ‘passive Fe-Mn oxidation’ is not simple, for several reasons:

- iron removal is not always easily accomplished. Some waters contain iron in a form that is slow to oxidize, or may be complexed with organic material that impedes oxidation and filtration. Precipitation may not occur if alkalinity is low;
- without a filtration step, much of the iron can remain suspended as

colloidal matter, even after oxidation;

- arsenite is not as strongly bound to iron as arsenate, if the waters contain mostly arsenite arsenic removal will be less efficient; and
- when water is stored in household containers, there is a high risk of bacterial contamination.

When considering passive Fe-Mn oxidation, particularly at the household level, careful pilot studies should be made using the local waters and local storage conditions, in order to assess the effectiveness of this technique, and the possibility of pathogenic contamination. It should be noted that chlorine addition would improve oxidation of both iron and arsenic, and would provide protection against bacterial growth. However, as discussed above, chlorination at the household level involves difficulties in ensuring the correct dose, and the potency of the chlorine agent.

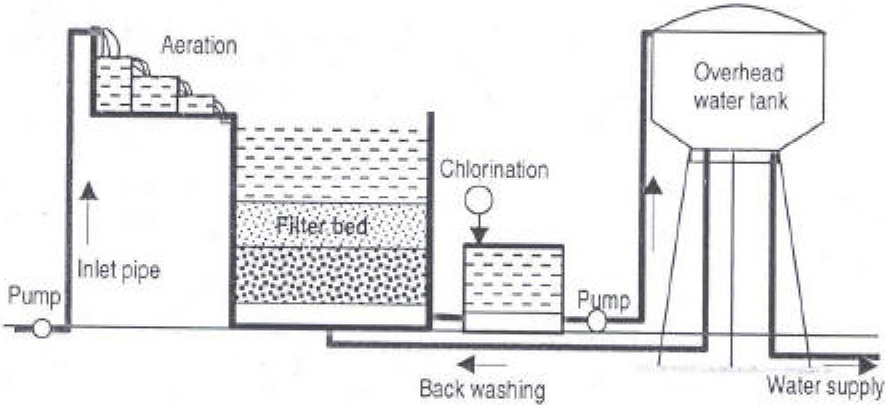
With support from the Dutch Government, the Department of Public Health Engineering of Bangladesh has constructed three arsenic removal plants in small municipalities. These plants are basically iron removal plants, and add no chemicals, but pump groundwater over a series of cascades to aerate the water. Filtration then removes the resulting iron and arsenic precipitate, and the water is chlorinated and stored in an elevated tank for distribution. Water stored in the tank is periodically used to backwash the filters. The waste water is stored in sludge ponds, and sludge is removed once or twice annually. Arsenic removal efficiency varies considerably, and seems to improve with higher iron levels:

Table 1 : Arsenic Removal in Three 18-DTP Plants

Municipality	Influent iron (mg/L)	Iron removal efficiency (%)	Influent arsenic (µg/L)	Arsenic removal efficiency (%)
Satkira Razzak	3.4	95	57.0	51
Satkira Polash	5.8	95	67.5	67
Manikganj	7.6	99	84.8	72

Source: (18-DTP, 1999)

Although removal rates are not very high, in all cases it is effective enough to bring waters into compliance with the Bangladesh drinking water standard of 50 µg/L. Plant managers experimented with addition of coagulants (4 mg/L $FeCl_3$) and oxidants (0.9 mg/L bleaching powder), but found that arsenic removal efficiency was not significantly improved.



Source: (Ahmed and Rahman, 2000)

Figure 3 : 18-DTP Arsenic Removal Plant

Sorption onto other metal oxides

Besides activated alumina, other metal oxides have strong affinities for arsenic, and can serve as effective sorbents, and in some cases as oxidants. Quartz is very poor at removing arsenic under most environmental conditions, because the mineral surface is negatively charged above a pH of 2. However, quartz sand, or indeed any other granular media, can be made highly sorptive by coating the grains with metal oxides. In recent years many researchers have used this principle to develop low-cost arsenic removal methods using locally available materials.Vaishya showed that sand from the Ganges river, which presumably is rich in iron coatings, could remove arsenite from solution, with a reported capacity of 0.024 mg/g. Removal was found to be pH-dependent, and best from pH 7-9 (Vaishya and Agarwal, 1993). Joshi and Chaudhuri showed that iron oxide coated sand (IOCS) is able to remove both arsenite and arsenate. A simple fixed bed unit was able to treat about 160-190 bed volumes of water containing 1000 µg/L arsenite and 150-165 bed volumes of water with 1000 µg/L arsenate. Flushing with 0.2 N sodium hydroxide regenerates the media. The authors propose that this media would be very useful for domestic arsenic removal units (Joshi and Chaudhuri, 1996).

A similar coated sand material can be prepared using manganese dioxide instead of iron. Since MnO_2 is a good oxidant, this material can remove arsenite as well as arsenate. In fact, the treated sand was able to remove 80% of a 1 mg/L solution of arsenite within two hours, but slightly less than 70% of an equivalent solution of arsenate. A prototype household unit was developed, which could treat about 150 bed volumes of 1 mg/L arsenic (half arsenite and half arsenate) before breakthrough (Bajpai and Chaudhuri, 1999).

Greensand is a granular material composed of the mineral glauconite, which has been coated with manganese oxide. It is a natural zeolite, and has strong ion exchange properties, and will remove iron, manganese, arsenic, sulfide, and many other anions. Like manganese dioxide coated sand, greensand surface is strongly oxidizing, and is thus able to remove both arsenite and arsenate. The media is typically recharged by application of potassium permanganate, which not only reestablishes the oxidizing environment, but deposits a fresh layer of manganese oxide on grain surfaces (Ficek, 1996). Viraraghavan and others showed that greensand could reduce arsenite levels from 200 µg/L by about 40% in the absence of iron. When ferrous iron was also present, arsenite removal improved to above 80% (Subramanian et al., 1997; Viraraghavan et al., 1999). Little information is available about the capacity of greensand for arsenic removal, or the effects of pH or competing anions on arsenic removal.

Several proprietary iron-based adsorption materials have been developed recently. Granular ferric hydroxides are being used in full scale systems in Germany (Driehaus et al., 1998), and similar materials have been developed in Canada and the United States. These materials generally have high removal efficiency and capacity.

Sorption onto reduced metals

Most of the above processes rely on arsenate adsorption onto surfaces of metal oxides. However, arsenic also has a strong affinity to reduced metal surfaces, such as sulfides. A few researchers have taken advantage of this property to remove arsenic through reduction and sorption.

Lackovic and others have demonstrated that zero-valent iron filings can be used either in situ or ex situ to reduce arsenate, and produce ferrous iron. The ferrous ions precipitate out with sulfide, which is also added to the system. Arsenite is removed either through coprecipitation or adsorption onto pyrite. This system is promising for use in rural areas, because of the low cost of materials, and the simple operation. However, treated water is very high in ferrous iron, and must undergo iron removal treatment before distribution or consumption (Lackovic et al., 2000).

A similar system using zero-valent iron to treat water stored in individual homes was tested in Bangladesh and West Bengal (the so-called: three kolshi filter). Arsenic removal was approximately 95% for highly contaminated waters, containing 2000 µg/L arsenic in the presence of sulfate at pH 7. Removal is rapid, but if batches are left for too long, dissolved iron concentrations become unacceptably high (Ramaswami et al., 2000).

Ion exchange and adsorption

Ion exchange resins developed for removal of anions such as sulfate and nitrate have proven to be reasonably effective at removing arsenic, as discussed above. As materials engineering becomes more advanced, researchers are increasingly able to design novel ion-exchange materials with surficial properties that are particularly specific to arsenate. In particular, several researchers have found that copper-doped materials have a strong, specific affinity for arsenate (e.g. Rajakovic and Mitrovicm, 1992; Ramana and Sengupta, 1992; Lorenzen et al., 1995). Fryxell and others have developed a novel mesoporous silica sorbent which makes use of Cu(II)-based functional groups. This material has a higher ion exchange capacity (75 mg As/g) than conventional resins, and shows a stronger affinity for arsenate and chromate than for sulfate or nitrate. Therefore, unlike the conventional resins, these materials will not release chromatographic peaks of arsenic when exposed to high levels of sulfate (Fryxell et al., 1999).

While conventional synthetic ion exchange resins are the most commonly used media in ion exchange, costs are relatively high ($USD 2-5 per liter of wet resin). A variety of naturally occurring materials also have high ion exchange capacities, sometimes after chemical pretreatment. Many of these materials are not pure ion exchangers: some arsenic removal is through less reversible chemisorption. Especially in developing countries, researchers have been evaluating the potential of these materials for use as low-cost arsenic removal systems.

Zeolites are naturally occurring minerals with a crystalline structure characterized by large internal pore spaces. Accordingly, they have very large surface areas, and ion exchange capacities: zeolites were used extensively for water softening, before the development of synthetic resins with faster exchange rates, higher capacity, and longer life. A few arsenic removal studies have been conducted with zeolites.

Natural zeolite minerals such as clinoptilolite and chabazite have a strong affinity for both arsenite and arsenate. A chabazite filter was able to remove 1000 µg/L arsenate from over 235 bed volumes before arsenic was detected in the effluent (Bonnin, 1997). Adsorption of arsenate onto natural zeolites can be improved by organically modifying the zeolite structure (Misaelides et al., 1998).

Chitosan and chitin are natural polyaminosaccharides occurring in crustacean shells, that have good ion exchange properties. Shellfish wastes containing chitosan have been used to remove arsenic from water contaminated by mining wastes (Luong and Brown, 1984). Elson and others investigated a mixture of chitosan and chitin, and found a relatively low arsenic removal capacity of about 0.01 mg As/g (Elson et al., 1980).

In Situ arsenic immobilization

When arsenic is mobilized in groundwater under reducing conditions, it is possible to immobilize the arsenic by creating oxidized conditions in the subsurface. In Germany, in order to remediate an aquifer containing high-arsenite, high ferrous iron, low-pH groundwater, Matthess injected 29 tons of potassium permanganate directly into 17 contaminated wells, oxidizing arsenite, which coprecipitated out with ferric oxides. Mean arsenic concentrations were reduced by over 99%, from 13,600 to 60 µg/L (Matthess, 1981). More recently, atmospheric oxygen was used to reduce arsenic concentrations *in situ* from approximately 20 to 5 µg/L, while iron and manganese levels were also lowered (Rott and Friedle, 1999). Under reducing conditions, and in the presence of sulfur, arsenic can precipitate out of solution and form relatively insoluble arsenic sulfides

In situ immobilization has the great advantage of not producing any wastes that must be disposed of. However, experience is limited, and the technique should be considered with caution. Oxidants are by definition reactive compounds, and may have unforeseen effects on subsurface ecological systems, as well as on the water chemistry. Care must also be taken to avoid contaminating the subsurface by introducing microbes from the surface. Also, at some point pore spaces can become clogged with precipitates, particularly if dissolved iron and manganese levels are high in the untreated water.

SUMMARY

The Table 2 summarizes some of the key technologies for arsenic removal, with special reference to experiences gained from field level application. Research needs are also identified. Arsenic removal efficiency will vary according to many site-specific chemical, geographic, and economic conditions, so actual applications may vary from the generalizations listed below. Because of the many factors that can affect arsenic removal efficiency (including arsenic concentration, speciation, pH and co-occurring solutes), any technology should be tested using the actual water to be treated, before implementation of arsenic removal systems at the field scale.

Table 2 : Summary of Technologies for Arsenic Removal

Technology	Removal Efficiency		Institutional experience and issues
	As (III)	As (V)	
Coagulation with iron salts	++	+++	Well proven at central level, piloted at community and household levels. Phosphate and silicate may reduce arsenic removal rates. Generates arsenic-rich sludge. Relatively inexpensive.
Coagulation with alum	-	+++	Proven at central level, piloted at household levels. Phosphate and silicate may reduce arsenic removal rates. Optimal over a relatively narrow pH range. Generates arsenic-rich sludge. Relatively inexpensive
Lime softening	+	+++	Proven effective in laboratories and at pilot scale. Efficiency of this chemical process should be largely independent of scale. Chiefly seen in central systems in conjunction with water softening. Disadvantages include extreme pH and large volume of waste generated. Relatively inexpensive, but more expensive than coagulation with iron salts or alum because of larger doses required, and waste handling.
Ion exchange resins	-	+++	Pilot scale in central and household systems, mostly in industrialized countries. Interference from sulfate and TDS. High adsorption capacity, but long-term performance of regenerated media needs documentation. Waters rich in iron and manganese may require pre-treatment to prevent media clogging. Moderately expensive. Regeneration produces arsenic-rich brine.
Activated alumina	+/ ++	+++	Pilot scale in community and household systems, in industrialized and developing countries. Arsenite removal is poorly understood, but capacity is much less than for arsenate. Regeneration requires strong acid and base, and produces arsenic-rich waste. Long-term performance of regenerated media needs documentation. Waters rich in iron and manganese may require pre-treatment to prevent media clogging. Moderately expensive.
Membrane methods	-/ +++	+++	Shown effective in laboratory studies in industrialized countries. Research needed on removal of arsenite, and efficiency at high recovery rates, especially with low-pressure membranes. Pretreatment usually required. Relatively expensive, especially if operated at high pressures.
Fe-Mn oxidation	?	+/ ++/ +++	Small-scale application in central systems, limited studies in community and household levels. More research needed on which hydrochemical conditions are conducive for good arsenic removal. Inexpensive.
Porous media sorbents (iron oxide coated sand, greensand, etc.)	+/ ++	++/ +++	Shown effective in laboratory studies in industrialized and developing countries. Need to be evaluated under different environmental conditions, and in field settings. Simple media are inexpensive, advanced media can be relatively expensive.

Technology	Removal Efficiency		Institutional experience and issues
	As (III)	As (V)	
In-situ immobilization	++	+++	Very limited experience. Long-term sustainability and other effects of chemical injection not well documented. Major advantage is no arsenic-rich wastes are generated at the surface, major disadvantage is the possibility of aquifer clogging. Should be relatively inexpensive.

Key:	
+++	Consistently > 90% removal
++	Generally 60 – 90% removal
+	Generally 30 – 60% removal
-	< 30% removal
?	Insufficient information

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